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REPORT

ON AN EXAMINATION

OF

SCHUTZENBERGER'S PROCESS,

FOR THE ESTIMATION OF

DISSOLVED OXYGEN

IN

THAMES WATER.

BY

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Report on an Examination of Schutzenberger's Process for the Estimation of Dissolved Oxygen in Thames Water.

Introduction.

My Lord,—In my last report to the Board on the question of the determination of dissolved oxygen in the river water, dated December 29th, 1888, I pointed out that the method now in use at Crossness (as described by Dr. Dupré) is vitiated by a serious source of error, viz., the effect of diffusion. On this important subject my assistant, Mr. Joseph Lunt, B. Sc., has now completed an exhaustive series of experiments in my Laboratory, the more important results of which I now beg to lay before the Board.

Diffusion

I stated that when aërated water is introduced into an atmosphere of hydrogen, as in the present method, the dissolved oxygen immediately begins to leave the liquid and diffuse into the gas above it. Experiment proves that in a very few minutes all the oxygen may in this manner be lost by simple exposure to hydrogen. In the method now in use, this rapid diffusion is arrested at some intermediate stage by the addition of hyposulphite, which combines with the oxygen remaining undiffused.

Effects of diffusion.

Upon the *rapidity* with which the hyposulphite is added, depends the amount of oxygen found by the titration. A significant fact was always observed after a titration had been performed, viz., that the yellow liquid produced during the analysis quickly regained its former blue colour on standing. The true interpretation of this well-known fact has not hitherto been given, and is simply that the diffused oxygen begins to be re-absorbed by the sensitive yellow liquid, and the consequent oxidation produces the blue colour.

To illustrate the effect of diffusion, I quote one out of many series of experiments made on the same sample of water by varying the exposure in each case. The numbers represent the relative amounts of oxygen found.

7·70	Titrated *at once* quickly, carefully at the last.
6·05	Titrated drop by drop, after standing one minute.
3·90	Titrated drop by drop, after standing in a current of hydrogen one minute.
0·95	Exposed 2½ minutes in a current of hydrogen.
0·35	Exposed 4 minutes in a current of hydrogen.

Hence any intermediate result between 7·70 and 0·35 is obtainable by stopping the diffusion at intermediate stages, and this quite sufficiently indicates the serious nature of the error due to diffusion.

Method of preventing diffusion.

I pointed out, also, a means by which diffusion could be prevented, viz., by introducing the water to be examined *beneath the surface* of a liquid containing a known quantity of hyposulphite, together with a little reduced indigo carmine as an indicator.

The hyposulphite effectually de-aërates the water before its exposure to hydrogen, in which gas the estimation must perforce be made, by combining with the oxygen, and so preventing its diffusion.

This last method of carrying out the estimation has been compared with the absolute process, viz., the extraction of the dissolved gases by boiling in vacuuo and their subsequent analysis.

Apparatus for absolute process.

A special apparatus for this purpose has been devised by my assistant, and this is figured and described in the appendix, together with the method of using it.

This comparison shows that diffusion is not the only difficulty which has to be contended with, for the impure nature of the water, containing as it does large amounts of organic and mineral matter, renders the volumetric process not perfectly accurate. This disturbing influence, however, is more constant than the last, and samples of impure water are found to yield fairly accurate results.

Further experiment may suggest a means of estimating and making a correction for this error, but in the meantime I should recommend the process described in detail later to be adopted as giving approximate results.

Results of the Examination of Water by the Absolute Method.

Five experiments made by this method on distilled water saturated with air at 10° C. gave, after correction for the varying atmospheric pressure—

Nitrogen	Difference from Mean	Oxygen	Difference from Mean
15·25	—·02	7·76	—·01
15·33	+·06	7·73	—·04
15·37	+·10	7·75	—·02
15·23	—·04	7·83	+·06
15·19	—·08	7·81	+·04
Mean 15·27 cb. c. per litre		Mean 7·77 cb. c. per litre of water	

These numbers show this method to be an accurate one.

Six samples of river water from Crossness have been examined by this method and also by the volumetric method.

The following are the results in cubic centimetres of gas per litre of water—

	March 4th	5th	6th	7th	8th	9th
Nitrogen	17·08	17·58	17·60	17·46	*15·96	16·96
Oxygen	2·51	0·59	0·13	1·06	4·36	4·68
Carbonic acid	14·00	15·29	15·77	14·51	*26·18	15·13
Total gas	33·59	33·46	33·50	33·03	46·50	36·77

Four samples of river water taken at Richmond-bridge gave.

February	19th	20th	21st	22nd
Nitrogen	17·14	16·74	16·23	16·31
Oxygen	8·37	8·00	7·75	8.05
Carbonic Acid	7·35	7·18	7·74	6·23
Total Gas	32·86	31·92	31·72	30·59

Water at Richmond and Crossness compared.

A comparison of these numbers is interesting as showing the great diminution in the oxygen, and the corresponding increase of the carbonic acid at Crossness, as compared with the water at Richmond, and it is well to remember that this excess of carbonic acid represents an equal volume of oxygen which has been absorbed in the natural purification of the river.

The inert nitrogen undergoes little variation except on March 8th, when the abnormally large proportion of carbonic acid, due to the rapid oxidation by the newly-

Carbonic acid determination.

acquired oxygen in the rain water, accounts for the expulsion of part of the nitrogen. Thus the carbonic acid determination becomes of importance as giving an indication of the amount of recently oxidised organic matter, and samples of water from Crossness might with advantage be examined from time to time by the absolute method.

Effect of diffusion on the gases in the river.

The natural tendency of such impure waters, especially those of March 5th, 6th, and 7th, containing little oxygen (independently of the action of organisms), is to lose the excess of carbonic acid by diffusion into the air, and to regain by atmospheric aëration the original proportion of oxygen shown in the Richmond water.

Whilst speaking of the absorption, by the impure water at Crossness, of the oxygen naturally dissolved in the purer water higher up the river, it may be well to obtain an idea of the action exercised by a heavy fall of rain on the natural purification of the river, as compared with the artificial addition of oxygen by means of manganate of soda.

For this purpose the sum of money may be calculated which must be spent in manganate to give to the river as much oxygen as is dissolved in the fresh water coming over Teddington Weir *in one day*. On November 27th, 1883, 4,187,500,000 gallons of water passed over the Weir, and this may be supposed to contain 7cc. of oxygen per litre,* or 0·7 grains per gallon. This corresponds to 418,750 lbs., or nearly 187 tons of oxygen per diem, and this is equivalent to †7,713 tons of manganate, the cost of which, at £8 per ton, amounts to £61,704; this sum representing the purifying value of the fresh water flowing over Teddington Weir on this particular day, expressed in terms of the available oxygen contained in manganate of soda.

The average daily flow over Teddington Weir for July, 1886, was 596,000,000 gallons, equivalent to 59,600 lbs. or 26·6 tons of oxygen on the same basis. This is equivalent to 1,097¼ tons of manganate, or £8,778 per diem during July, 1886.

The flow of fresh water over the Weir is seldom below one-third this amount.

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*The water at Richmond in February contained 8cb.c. per litre.]

† To furnish 1 ton of oxygen, 41¼ tons of manganate are required.

Comparison of the Volumetric with the Absolute Method of Analysis.

The six samples before mentioned, taken at Crossness gave results as follows—

Oxygen in cubic centimetres per litre.

Absolute Method	2·51	0·59	0·13	1·06	4·36	4·68
Volumetric Method	2·64	0·85	0·30	1·45	4·54	5·20
Difference	+·13	+·26	+·17	+·39	+·18	+·52

The result of the volumetric process, as afterwards described in detail, when carried out on Crossness water, is thus always rather too high in the above samples, the mean difference being only 0·28 cb. c. per litre.

As I have already pointed out, further experiment may suggest a means of estimating and making a correction for this difference in each sample.

The samples examined gave a wide range of oxygen numbers, and the comparisons are thus rendered all the more valuable ; and the results indicate that the process gives fairly accurate results, even when the water contains only minute quantities of oxygen.

I next describe the apparatus and method proposed to be used hereafter.

Apparatus and method to be adopted.

The apparatus differs considerably from that at present in operation ; it is figured so clearly in Figure 1* that very little description is needed. The figure shows an arrangement for a continuous supply of pure hydrogen, by the action of dilute sulphuric acid on zinc. The gas is first passed through wash bottles containing caustic soda, and then through two long tubes containing beads moistened with an alkaline solution of potassium pyrogallate, to absorb every trace of oxygen, an arrangement being made by which the beads may be re-moistened with fresh pyrogallate from the reservoirs beneath the tubes, and the liquid raised by hydrogen pressure.

The pure gas is supplied continuously, as shown in the figure—(1) To the stock bottle of hyposulphite. (2) To the hyposulphite burette. (3) To the wide-mouthed bottle of 200 cb. c. capacity, in which the estimation is made. The outlet for the gas is through the water contained in the small tube, shown beside the bottle.

The hypo-burette is supplied by a glass syphon which should join the stock bottle with as little indiarubber as possible. The indigo carmine solution is supplied from a large bottle, not shown in the figure, in a similar manner. The water to be tested is contained in a Winchester quart bottle, furnished with a syphon communicating with the lower part of a large burette. In this manner the water can be introduced into the titration bottle, without exposure to air, the use of hydrogen as before practised, being of course inadmissible. An analysis is performed as follows—

20 cb. c. of the water to be tested are run into the titration bottle filled with pure hydrogen, and a measured quantity of indigo carmine added, sufficient to produce a good yellow colour when reduced.

The blue liquid is rinsed round in a current of hydrogen for three minutes; this effectually frees the liquid from all dissolved oxygen, by diffusion.

The current of gas is stopped by turning the tap beside the burettes, and hyposulphite carefully added until an exact decolourisation takes place, care being taken not to overstep the point.

A measure of hyposulphite is now added to the yellow liquid, sufficient to combine with the oxygen dissolved in from 50 to 100 cc. of the water under examination. The water is at once run in, with constant rinsing, until a permanent blue colour is produced. The water being introduced by a capillary tube passing to the bottom of the bottle, first comes in contact with hyposulphite and reduced indigo, which immediately combine with the oxygen, and so prevent diffusion. The blue colour thus produced deepens on standing, and a further addition of hyposulphite is made, sufficient to give a permanent yellow colour.

The sum of the volumes of hypo added in the second and third additions is taken as being equivalent to the oxygen dissolved in the volume of water added to the yellow liquid.

Care must be taken that all the tubes are tightly fitting, and every precaution taken to exclude outside air. As few indiarubber joints as possible should be made, and these wired and water-luted.

In cases where the water contains only small amounts of oxygen, say below 1·5 cb. c. per litre, the excess of hypo may be omitted, the reduced indigo carmine alone being sufficient to combine with all the oxygen. When this method is used, care must be taken that the volume of hypo required for the first decolorisation is at least twice that requisite after the introduction of the water.

An exactly similar experiment is now made with distilled water aërated at a known temperature and pressure, and the result calculated from the hyposulphite value thus obtained, Bunsen's coefficient of absorption being used.

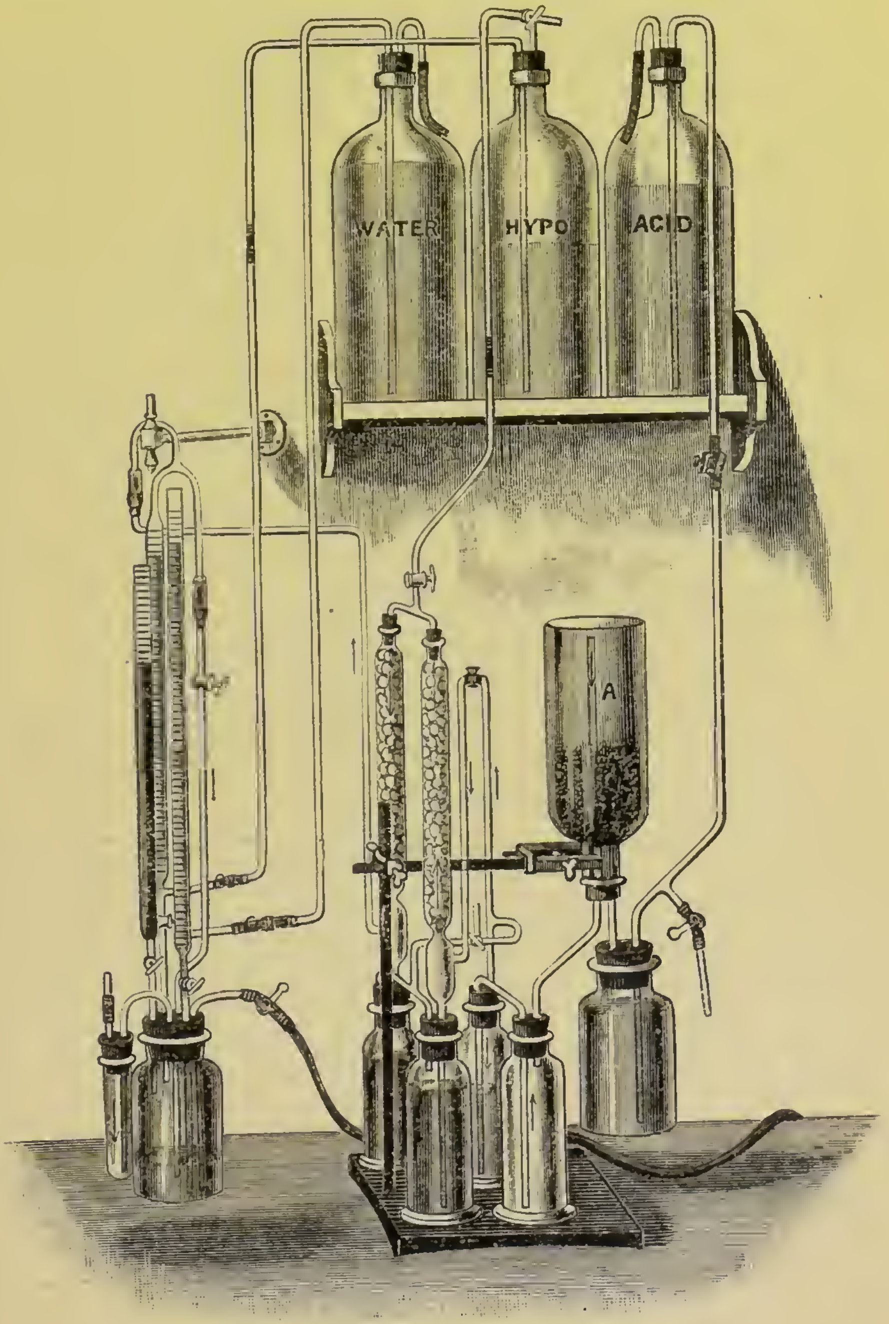

FIGURE I.

Standardisation of the Hyposulphite.

Three methods can be employed. (1) The copper method. (2) The indigo method. (3) The aërated distilled water method.

(1) The copper method gives results which are far too low, and so cannot be used.

(2) The indigo method is a convenient one, when once the value of the solution has been carefully found by the third method, and may be used.

(3) The aërated distilled water method.

A few words are requisite about the oxygen value of distilled water aërated at a known temperature and pressure. The five determinations previously given, for distilled water aërated at 10° C. and 760 m.m. bar show 7·77 cb. c. of oxygen per litre.

The use of this figure gives too high results for Crossness water because of the error due to the impurity of the water. Bunsen's coefficient gives 6·81 cb.c.'s per litre, and the use of this lower figure counteracts in some measure, but not entirely, this error; and this number, with the corresponding ones for each temperature, should be used until by further experiment the error can be estimated and allowed for.

The hyposulphite should be standardised daily, as its strength undergoes a gradual diminution, even when kept in hydrogen, as in the figure.

I have the honour to remain, my Lord,
Yours faithfully,
HENRY E. ROSCOE.

To Lord Magheramorne,
Chairman, Metropolitan Board of Works.

APPENDIX.

Apparatus for the Extraction and Analysis of the Gases dissolved in Water, and the method of using it.

The apparatus in which the gases are extracted from the water under examination is shown in figure II. It is first completely exhausted of air by pumping about 200cb.c. of water into the large bolt-head A, of about three litres capacity, filling the side tube F with the water to be examined from the bottle S.

The lamp beneath A is lit, and the apparatus exhausted of air by the air-pump shown in the figure.

When the exhaustion has proceeded as far as possible by the air-pump, the three-way tap beneath B is turned to communicate with the mercury reservoir R, the mercury rises in the tube beneath B, and is allowed to flow, by a suitable turn of the tap, into the U tube, thus shutting off communication with the air.

The three-way tap beneath B is kept closed during the rest of the operation, and the outlet is sealed by mercury. The boiling is continued, and the vapour drives all the gas before it into D and E.

The tap beneath E, in the glass bowl full of water, is opened, and the mercury reservoir raised. Mercury rises in E, and all the air which has there collected is driven out through the capillary barometer tube, and the mercury trough T. On lowering the reservoir a vacuum is produced in E. The contents of D are transferred to E and thence out by the trough. This is repeated three or four times until the contents of D and E, when condensed into the capillary barometer tube, show no gas.

The apparatus is now ready for the introduction of the water to be examined, the tap communicating with S is opened, and the water rushes into the vacuous space with an immediate escape of the greater part of the gases previously held in solution. When a sufficient quantity of water has been introduced, about 1500-1700 cb. c. the tap is shut off, and the flame placed beneath the bolt-head A.

The gases are given off with brisk effervescence, and make their way into E, free from water, which has condensed in its passage through B, C, and D. The dry gas is passed over into the gas tube G, full of mercury, by raising R, and on lowering it more gas enters the

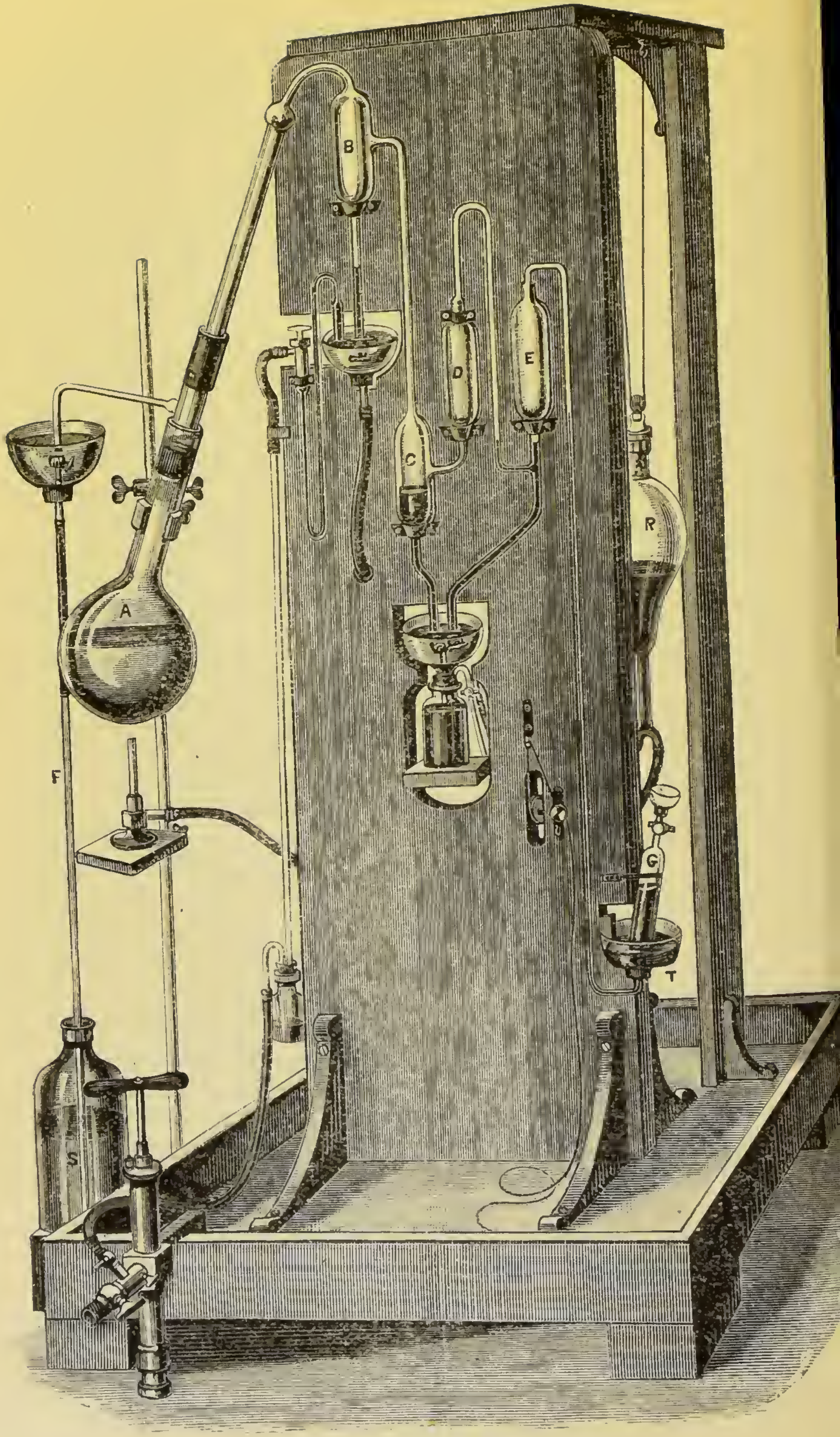

Figure II.

vacuous space, and is driven over like the last. This is done several times until water condenses in the capillary tube leading from D to E, when a brisk boiling is kept up for a few minutes, the condensed water is drawn back into D, by raising the mercury, connecting the water in D and E, and drawing it back into D by slowly lowering the Reservoir R. The gas is passed out, and this operation repeated until no further gas is obtained.

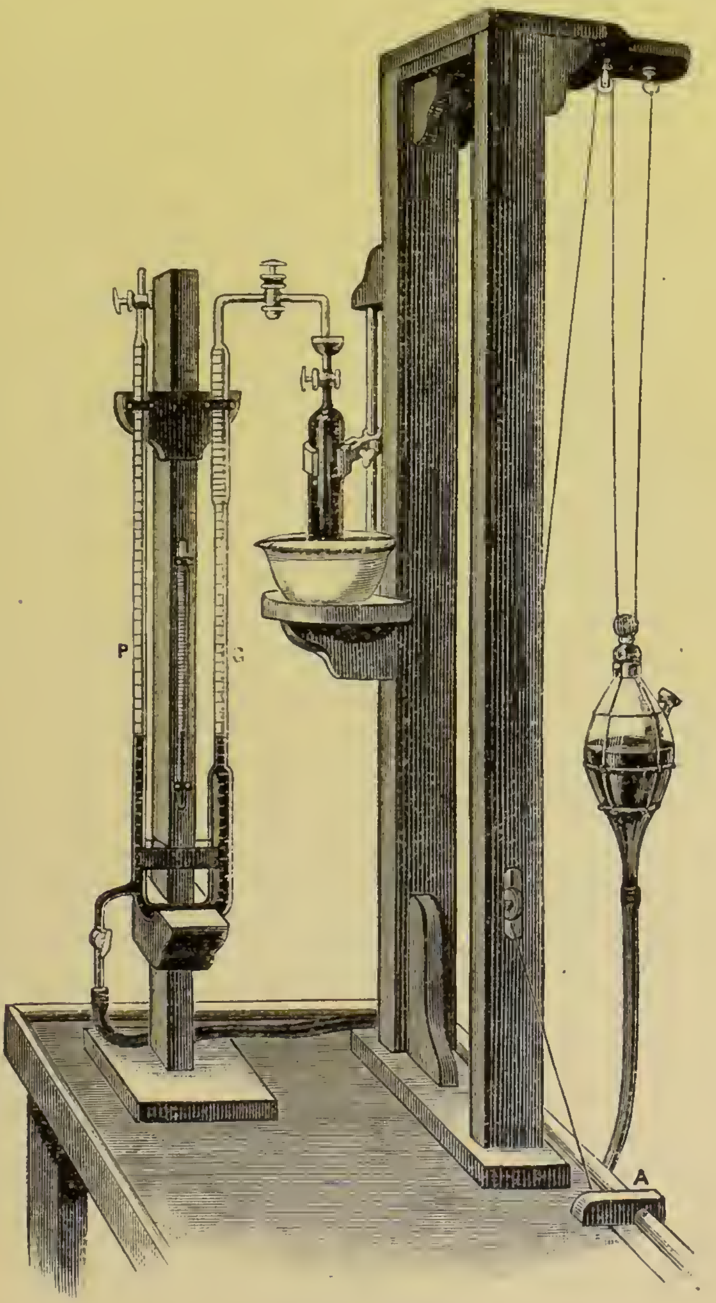

Figure III.

Carbonic acid continues to come off even after all the nitrogen and oxygen have been collected, and in impure waters the last portions of gas need not be dealt with, unless an accurate measure of carbonic acid is needed. The four glass taps and the two joints are surrounded by water, so that no leakage from the atmosphere can possibly take place, although a vacuum is produced in the apparatus.

The exhaustion of the apparatus occupies about 25 minutes, and the extraction of the gases from a sample about 20 minutes. The gases collected in G are now transferred to the apparatus shown in Figure III, where they are analysed, by absorbing the carbonic acid by caustic potash solution, and the oxygen by alkaline potassium pyrogallate.

The apparatus is a modified form of Frankland's gas apparatus.

The important point is, that the two measurements which require great accuracy are made in the narrow part of the gas tube G, thus diminishing the experimental error of each reading. The nitrogen is measured at the upper part of the narrow tube, and the nitrogen and oxygen together at the lower part. The total gas, which gives the volume of carbonic acid, is measured on the lower and wider part of the gas tube.

The tube P is for the purpose of measuring the pressure; it is marked in millimetres, and the readings are taken by a telescope not shown in the figure.

The piece A slides along the edge of the table, and by its means the gas can be adjusted to the greatest nicety, to the marks on the gas tube, by the slight raising or lowering of the mercury reservoir. The five results given for distilled water obtained by this apparatus show a maximum variation from the mean, nitrogen ·1 cb. c., oxygen ·06 cb. c. per litre of water.

(Signed) H. E. ROSCOE.

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